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DOI link to article:

<http://dx.doi.org/10.1063/1.4938247>

Date deposited:

04/01/2016

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Citation: *The Journal of Chemical Physics* **143**, 244309 (2015); doi: 10.1063/1.4938247

View online: <http://dx.doi.org/10.1063/1.4938247>

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The pure rotational spectra of the open-shell diatomic molecules PbI and SnI

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(Received 2 October 2015; accepted 2 December 2015; published online 28 December 2015)

Pure rotational spectra of the ground electronic states of lead monoiodide and tin monoiodide have been measured using a chirped pulsed Fourier transform microwave spectrometer over the 7–18.5 GHz region for the first time. Each of PbI and SnI has a $X^2\Pi_{1/2}$ ground electronic state and may have a hyperfine structure that aids the determination of the electron electric dipole moment. For each species, pure rotational transitions of a number of different isotopologues and their excited vibrational states have been assigned and fitted. A multi-isotopologue Dunham-type analysis was carried out on both species producing values for Y_{01} , Y_{02} , Y_{11} , and Y_{21} , along with Λ -doubling constants, magnetic hyperfine constants and nuclear quadrupole coupling constants. The Born-Oppenheimer breakdown parameters for Pb have been evaluated and the parameter rationalized in terms of finite nuclear field effects. Analysis of the bond lengths and hyperfine interaction indicates that the bonding in both PbI and SnI is ionic in nature. Equilibrium bond lengths have been evaluated for both species. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4938247>]

INTRODUCTION

In recent years, there have been a number of spectroscopic and theoretical studies on heavy relativistic open-shell diatomic molecules such as PbF due to their possibility of possessing a ground state that is particularly sensitive to an electron electric dipole moment (*e*EDM), d_e , thus making these the molecules of interest in order to study charge parity violation theory.¹ The notion of the *e*EDM was first presented in a wave-equation by Dirac in 1928 and then later Purcell and Ramsey discussed the possibility of the *e*EDM being evidence for the parity violation theory.^{2,3} Work by Hudson *et al.* in 2011 used YbF to determine a value of d_e which set the new upper limit to $|d_e| < 10.5 \times 10^{-28}$ e cm with a 90% confidence and indicates that the electron is spherical and not aspheric as predicted.^{4,5}

The molecule PbF was also of interest due to its small *g*-factor; a constant which describes the magnetic moment of the molecule. In a molecule with orbital angular momentum this *g*-factor depends on the type of coupling between different components of angular momenta. To date only PbF and PbCl have been studied using high-resolution spectroscopy allowing information regarding their hyperfine structure to be obtained and examined to find suitable energy levels for the study of charge parity violation.^{6–8} With the aim of expanding our knowledge of metal halides that have potential to be used for the study of the *e*EDM, we have carried out a microwave spectroscopy investigation of PbI and SnI.

The electronic structure of the system PbI has been the subject of many spectroscopic studies since the 1940s. More recent studies include the work by Ziebarth *et al.* which reported vibrational constants (ω_e and $\omega_e x_e$) as well as spin-orbit coupling within the $^2\Pi$ ground state of the lead monohalides (PbF, PbCl, PbBr, and PbI).⁹ In this study, PbI was generated by reacting PbI₂ with H atoms via a discharge source. The emission signal was then recorded using a Fourier transform infrared spectrometer. Rodriguez *et al.* reported an absorption and emission UV-spectroscopic study on the A, B, D, and E electronic states of PbI by photodissociation of PbI₂.¹⁰ They give values for the vibrational constants (ω_e and $\omega_e x_e$) of the ground state and the A electronic state. A number of computational chemistry studies have also been carried out on PbI. Benavides-Garcia and Balasubramanian carried out calculations on the equilibrium structures and the associated potential energy surface of a number of electronic states of PbI,¹¹ while Shimizu and Frenking calculated structures of different lead-halide clusters including PbI.¹² Li *et al.* and Stoll *et al.* performed a theoretical study on the structures and dissociation energies of all the lead monohalides.^{13,14} In terms of microwave spectroscopy, no studies on PbI have been reported to date and only investigations on PbF and PbCl have been published.^{6,8} For the PbF study, rotational, centrifugal distortion, Λ -splitting, and hyperfine constants were obtained for ²⁰⁴PbF, ²⁰⁶PbF, ²⁰⁷PbF, and ²⁰⁸PbF in the ground vibrational state.⁶ For the PbCl study, only spectroscopic parameters of the ²⁰⁶Pb^{35/37}Cl and ²⁰⁸Pb^{35/37}Cl isotopologues in their ground vibrational states were obtained.⁸

For SnI, there have been a number of studies since the first recorded electronic spectrum in 1934 by Howell and Rochester.¹⁵ Oldershaw and Robinson reported the B² Σ^+ state

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within the recorded absorption spectra of SnI which was generated by flash photolysis of SnI₄.¹⁶ Murty *et al.* observed the A $^2\Sigma^+$ state of SnI in emission band spectra.^{17,18} Iacocca *et al.* and Oldershaw and Robinson reported studies on the C, D, E, F, G, and H electronic states from the emission spectra of SnI with Iacocca *et al.* giving an estimate of the X $^2\Pi_{3/2}$ component of $\sim 2684\text{ cm}^{-1}$.^{19,20} Li *et al.* also investigated SnI in their computational study on group IV halides.¹³ Microwave spectra have not been reported for SnI, while SnCl has been studied using both cavity Fourier Transform microwave (FTMW) and chirped pulsed FTMW spectroscopy, with SnCl generated via the laser ablation of tin in the presence of Cl₂ gas. This allowed the determination of rotational, centrifugal distortion and hyperfine constants for $^{120}\text{Sn}^{35/37}\text{Cl}$, $^{118}\text{Sn}^{35}\text{Cl}$, and $^{116}\text{Sn}^{35}\text{Cl}$.²¹

In this investigation, the chirped pulsed Fourier Transform microwave (CP-FTMW) spectra of the open shell molecules PbI and SnI will be analysed in their ground electronic state (X $^2\Pi_{1/2}$) for the first time and rotational, centrifugal distortion, and hyperfine constants will be evaluated and interpreted.

EXPERIMENTAL

Spectra were collected using a CP-FTMW spectrometer which has been described in recent literature.^{22,23} In order to generate either PbI or SnI, a gas mixture of $\sim 1\%$ CF₃I in argon at 6 bars pressure is prepared. This sample is introduced into a vacuum chamber using a pulsed valve and undergoes supersonic expansion. The repetition rate of valve pulses is approximately 1.05 Hz. The expanding gas sample passes over the surface of a metal rod from which material is ablated using the focussed pulse (10 ns, 20 mJ/pulse) from a Nd:YAG laser operating on the 2nd harmonic (532 nm). The rod target is composed of the pure ($>99.9\%$) metal, either Pb or Sn as appropriate.

The target rod is continually rotated to ensure a fresh surface of the metal is exposed to each laser pulse, giving improved shot-to-shot reproducibility. A more detailed description of the nozzle and ablation source can found elsewhere.²² Monohalides of tin and lead as well as many other products from precursor fragmentation and reaction are generated during the ablation process. The expanding gas (rotational temperature $\sim 2\text{ K}$) pulse propagates perpendicular to a chirped microwave pulse introduced from a broadband horn antenna which is timed to coincide with the passage of the gas pulse. Where rotational transitions are resonant with the introduced microwave pulse between 7 and 18.5 GHz, molecules within the expanding jet become rotationally polarised. The subsequent free induction decay (FID) of the molecular emission, 20 μs in duration, is detected by a second horn antenna positioned directly opposite the first.

Multiple FIDs are digitized and recorded on a fast digital oscilloscope (Tektronix, DPO71254) before these time-domain data are averaged and Fourier transformed to obtain the frequency domain spectrum. In order to maximise the duty cycle of the instrument, and given that each gas pulse endures for $\sim 200\text{ }\mu\text{s}$, the cycle of (i) chirped microwave pulse excitation and (ii) detection and recording of the FID is repeated eight times per gas valve pulse. The frequency

domain spectrum was obtained by averaging 600k FIDs for PbI and 1M FIDs for SnI. The baseline resolution was improved by applying a Kaiser-Bessel function during the Fourier transformation with the linewidth (FWHM) after the application of the window function was estimated to be 120 kHz. The current experiment has no Zeeman coils to eliminate the effects from the earth's magnetic field; the resolution was such that no Zeeman splittings were observed. The dephasing time is about 10 μs (at $\nu = 12\text{ GHz}$). In both the PbI and SnI spectra, the dominant features belong to transitions of CF₃I which are well known since the first report of its microwave spectrum in 1952 by Sheridan and Gordy.²⁴ To aid in the initial assignment of each spectrum, the transitions of all peaks associated with CF₃I, its isotopologues and excited vibrational states were removed by recording a spectrum of CF₃I on its own and subtracting it from the recorded spectra of PbI and SnI.

The spectral analysis program PGOPHER was used to display, simulate, and to fit the recorded spectra.²⁵ The final fits were carried out using the Pickett software, SPFIT. This included carrying out fits of equilibrium parameters in addition to an isotopically invariant analysis of both PbI and SnI.^{26,27}

RESULTS AND DISCUSSION

Spectroscopic analysis of PbI and SnI

Lead has four naturally abundant isotopes, ^{204}Pb (1.4% natural abundance), ^{206}Pb (24.1%), ^{207}Pb (22.1%), and ^{208}Pb (52.4%), while iodine has only one isotope (^{127}I) so it is assumed that spectral features from ^{206}PbI , ^{207}PbI , and ^{208}PbI will be observed along with lines corresponding to lead monofluoride (PbF). As the frequencies of the PbF transitions are known, these can be easily separated from the spectral features belonging to the different isotopologues of PbI.⁶ Although the aim of this work is to investigate PbI and SnI, a number of other Pb and Sn containing species will also be present. It will be shown that rotational transitions are present for many different vibrational states and isotopologues of PbI and SnI such that assignment of the observed spectra is a challenging task. One advantage of broadband rotational spectroscopy is that patterns can be readily distinguished in broadband spectra because (i) many transitions can be measured and compared during a single experiment and (ii) the displayed intensities of transitions depend almost entirely on fundamental physical properties of the expanding gas and the detected molecules rather than any frequency-dependent instrumental parameter. This capability will be of high value during the present work.

The ground electronic state of PbI has been shown to be $^2\Pi_{1/2}$.⁹ The Hamiltonian used to fit the data is given by

$$H = H_{SO} + H_R + H_{LD} + H_{MHF} + H_{Q(I)}, \quad (1)$$

where H_{SO} is the electronic spin-orbit interaction, H_R is the rotational Hamiltonian including centrifugal distortion, H_{LD} is the Λ -doubling parameters, H_{MHF} is the magnetic hyperfine interaction terms, and $H_{Q(I)}$ is the nuclear electric quadrupole Hamiltonian due to the iodine nucleus ($I = 5/2$). Each is

defined as

$$H_{SO} = AN_Z S_Z + \frac{1}{2} A_D [N_Z S_Z, N^2], \quad (2a)$$

$$H_R = BN^2 - DN^4, \quad (2b)$$

$$H_{LD} = -\frac{p}{2} [N_+ S_+ + N_- S_-] + \frac{q}{2} (N_+^2 + N_-^2), \quad (2c)$$

$$H_{MHF} = aI_Z N_Z + \frac{d}{2} (I_+ S_+ + I_- S_-), \quad (2d)$$

$$H_{Q(I)} = \frac{\frac{3}{2} eQq_1}{2I(2I-1)} \left[I_Z^2 - \frac{1}{3} I^2 \right]. \quad (2e)$$

The initial rotational constant of PbI was taken from the work of Benavides-Garcia and Balasubramanian, while the values of p from the work on PbF and PbCl were used to predict a suitable value for the Λ -doubling constant of PbI.^{6,8} From these initial values a number of spectral features were identified to be belonging to PbI and a fit based on Hund's case (b) was used throughout. Assignments and fits were first made using PGOPHER, an interactive spectral fitting program developed by Colin Western.²⁵ Subsequently, Pickett's SPFIT program was used in the final fits since it was able to carry out mass invariant fits and fits to equilibrium parameters.^{26,27} Line centres can typically be measured by microwave spectroscopy with a precision that approaches 10% of the FWHM linewidth. However, Zeeman splittings are expected for a molecule in a $^2\Pi_{1/2}$ electronic state and these could not be distinguished for either PbI or SnI at the resolution of the present experiments. The unresolved hyperfine structure will have a distorting effect on the observed line profiles and slightly reduce the precision with which the line centres are measured. A frequency uncertainty of 20 kHz, slightly greater than 10% of the (FWHM) linewidth and equal to the point spacing in the power spectrum, is therefore assumed for measured transitions in the spectra of PbI and SnI. Assignment and transition

frequencies can be found in the supplementary material,²⁸ where each transition is assigned based on the following set of quantum numbers: $N'', p'', v'', J'' + \frac{1}{2}, F'' \leftarrow N', p', v', J' + \frac{1}{2}, F'$.²⁸ Λ -doubling results in the formation of e and f states, where the parity in SPFIT is given by $p = (-1)^{J-\frac{1}{2}}$ and $p = (-1)^{J+\frac{1}{2}}$, respectively. For the iodine nucleus, which has a nuclear spin of $5/2$, it can couple with \mathbf{J} with the following coupling scheme $F = J + I \dots |J - I|$, where for rotational transitions $\Delta F = 0, \pm 1$. For ^{207}PbI , where the ^{207}Pb nucleus has a spin of $I = 1/2$, the coupling scheme changes to $F_1 = J + I \dots |J - I|$, $F_{\text{Total}} = F_1 + I_{\text{Pb}} \dots |F_1 - I_{\text{Pb}}|$.

Transitions from $J = 3.5 \rightarrow 4.5$ to $J = 9.5 \rightarrow 10.5$ were observed and assigned to ^{206}PbI , ^{207}PbI , and ^{208}PbI . Figures 1(a)-1(c) show different parts of the recorded spectrum of PbI highlighting the different vibrational states, the different isotopologues observed and the hyperfine structure.

For each set of transition frequencies associated with a vibrational state of a given isotopologue of PbI, the rotational constant, B , centrifugal distortion constant D_J , Λ -doubling constant p , magnetic hyperfine constants a and d (for the ^{127}I and ^{207}Pb nuclei), and the nuclear electric quadrupole coupling constant (NQCC), $eQq(I)$ were evaluated. Due to strong correlation with p , the Λ -doubling constant q was fixed to zero in each fit, while the magnetic hyperfine constants c and b_F and the higher order NQCC $eQq_2(I)$ could not be determined and were also fixed to zero. The spin-orbit coupling constant A and its centrifugal distortion correction term A_D were also not determined as only the $^2\Pi_{1/2}$ component was investigated and so A was held to the literature value for each isotopologue and A_D fixed to zero.⁹ In this study, the values of A and A_D have no influence on the fits since only the $^2\Pi_{1/2}$ component was investigated. For each set of transitions, the weighted non-linear least squares fit gave a RMS error less than 1 indicating that the fitted parameters modelled the

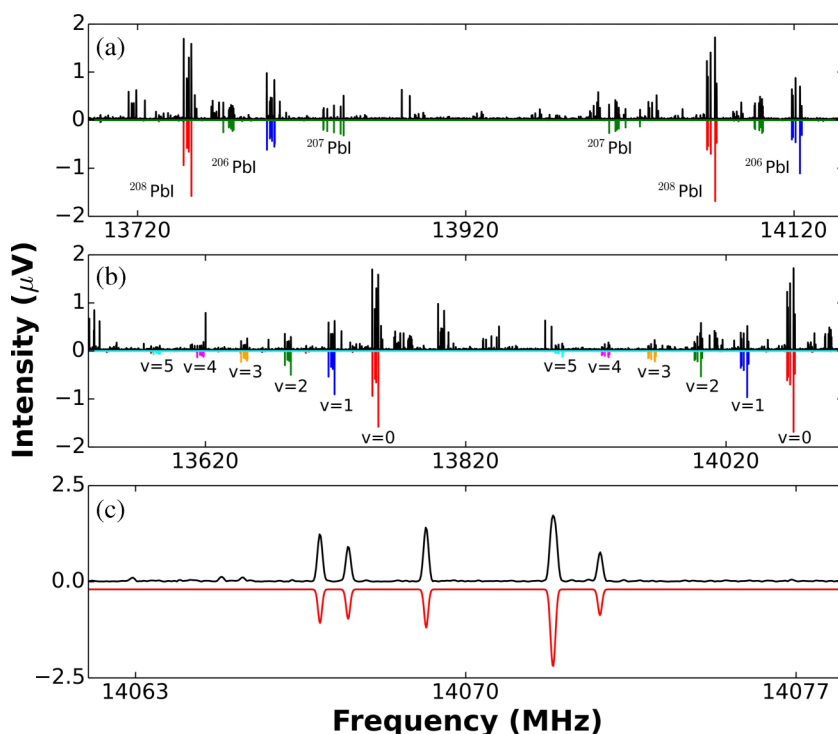


FIG. 1. Overview of the $J = 8.5 \rightarrow 9.5$ transition of PbI. (a) Different isotopologues observed for PbI (all in $v = 0$ state). (b) The vibrational states observed for ^{208}PbI . (c) An expanded section of the $J = 8.5 \rightarrow 9.5$ transition of ^{208}PbI showing the hyperfine structure. In each case, the black trace (top half of each panel) is the experimental data while the other coloured traces (bottom half of each panel) are simulations using the model Hamiltonian.

system extremely well. The individual fits for each vibrational state can be found in the supplementary material.²⁸

The fitted spectroscopic constants for ²⁰⁸PbI ($v = 0$ to $v = 5$), ²⁰⁷PbI ($v = 0$ to $v = 1$) and ²⁰⁶PbI ($v = 0$ to $v = 2$) were analysed to obtain equilibrium spectroscopic constants. The transition frequencies associated with each isotopologue of PbI (and SnI—see the section titled “Bond lengths of PbI and SnI”) were fitted to the standard Dunham expression using Pickett’s SPFIT program,

$$E_{v,J} = \sum_{i,j} Y_{ij} \left(v + \frac{1}{2} \right)^i j^j (J+1)^j. \quad (3)$$

In Equation (3), the Y_{ij} parameters are the Dunham parameters. The equilibrium parameters for the different isotopologues of PbI are given in Table I.

A similar analysis was carried out for the isotopologues and excited vibrational states observed for SnI since it also has a ²Π_{1/2} ground state. Tin has ten naturally abundant isotopes; however, only seven isotopologues of SnI would be observable with the conditions used: ¹¹⁶SnI (14.5% natural abundance), ¹¹⁷SnI (7.7%), ¹¹⁸SnI (24.2%), ¹¹⁹SnI (8.6%), ¹²⁰SnI (32.6%), ¹²²SnI (4.6%), and ¹²⁴SnI (5.8%). Spectral features from the isotopologues containing the $I = 0$ tin isotopes ¹¹⁶SnI ($v = 0$ to $v = 5$), ¹¹⁸SnI ($v = 0$ to $v = 7$), ¹²⁰SnI ($v = 0$ to $v = 9$), ¹²²SnI ($v = 0$), and ¹²⁴SnI ($v = 0$ to $v = 1$) were observed. Figure 2 shows the different vibrational states observed for ¹²⁰SnI

for the $J = 5.5 \rightarrow 6.5$ transition. No spectral features were observed from the isotopologues containing the $I = 1/2$ tin isotopes, ¹¹⁷Sn and ¹¹⁹Sn. The same Hamiltonian used for PbI was applied to SnI and the individual fits for each vibrational state can be found in the supplementary material.²⁸ As with PbI, the parameters related to spin-orbit coupling, A and A_D , for SnI were not determined as only the ²Π_{1/2} component was investigated and so A was held to the literature value for each isotopologue and A_D fixed to zero.²⁰ The typical RMS error for each of the weighted non-linear least squares fits was less than one indicating that the parameters associated with the Hamiltonian model the observed transition frequencies well. The same equilibrium analysis of the rotational, centrifugal distortion and the $eQq(I)$ constants was carried out as done with PbI and the results are listed in Table II.

Bond lengths of PbI and SnI

This is the first ever experimental determination of the bond lengths associated with a group 4 monoiodide species. A computational study by Li *et al.* at the CCSD(T) level of theory gave estimates of the bond lengths of SiI (243.7 pm), GeI (251.0 pm), SnI (269.7 pm), and PbI (278.0 pm), with the results for SnI and PbI being in good agreement with equilibrium values determined in this study of 270.32 pm and 279.76 pm, respectively (see Tables I and II).¹³ Other studies on PbI have

TABLE I. Derived equilibrium parameters for ²⁰⁸PbI, ²⁰⁷Pb, and ²⁰⁶PbI in the X ²Π_{1/2} electronic state.

Parameter ^a	²⁰⁸ PbI	²⁰⁶ PbI	²⁰⁷ PbI	Literature
Y_{01} /MHz	819.301 68(28)	822.319 42(32)	820.802 28(23)	
Y_{11} /MHz	−2.035 79(19)	−2.047 42(44)	−2.040 89(12)	
Y_{21} /kHz	0.276(32)	0.38(15)	...	
Y_{02} /Hz	−94.5(13)	−93.8(13)	−92.5(12)	
p_{00} /MHz	327.188 6(46)	328.427 2(46)	327.808 6(74)	
p_{10} /MHz	1.975 2(18)	2.015 5(32)	2.04(10)	
$a_{00}(I)$ /MHz	187.278(57)	187.130(72)	187.396(54)	
$a_{10}(I)$ /MHz	−0.786(34)	−0.608(66)	−0.578(64)	
$d_{00}(I)$ /MHz	239.494(10)	239.247(19)	239.744(26)	
$d_{10}(I)$ /MHz	−0.574(11)	−0.789(22)	−0.404(70)	
eQq_{00} /MHz	−700.741(52)	−701.460(93)	−703.861(62)	
eQq_{10} /MHz	−1.633(52)	−1.83(13)	...	
$a_{00}(\text{Pb})$ /MHz	4 729.59(22)	
$a_{10}(\text{Pb})$ /MHz	4.78(34)	
$d_{00}(\text{Pb})$ /MHz	6 322.32(64)	
$d_{10}(\text{Pb})$ /MHz	9.4(1.1)	
r_e /pm	279.760 409(48)	279.760 455(54)	279.760 511(39)	288.5, ^b 278.0 ^b 282.9, ^b 277.2 ^b 277.0 ^b 153, ^b 174 ^b 168, ^b 169 ^b
ω_e /cm ^{−1}	160.9(11)	162.4(11)	163.1(11)	161.0, ^c 160.3 ± 0.6 ^c
$\omega_e x_e$ /cm ^{−1}	0.323 2(31)	0.327 8(32)	0.329 5(30)	0.24 ± 0.03, ^c 0.287 ^c 20 486, ^b 16 937 ^b
D /cm ^{−1}	20 036(337)	20 117(342)	20 189(321)	14 518, ^b 23 954 ^b 16 088 ± 700 ^c
No. of lines	464	229	243	
RMS error	1.14	0.79	0.74	

^aThe numbers in brackets indicate one standard deviation.

^bReferences 11–14.

^cReferences 9, 10, and 43.

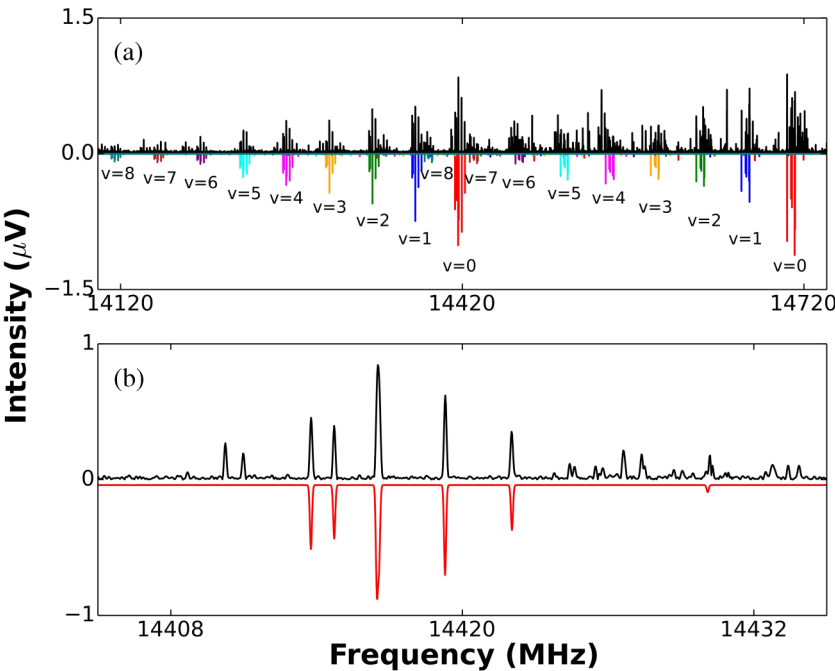


FIG. 2. (a) Overview of vibrational states observed for ^{120}SnI ($J=5.5 \rightarrow 6.5$). (b) An expanded section of the $J=5.5 \rightarrow 6.5$ transition of ^{120}SnI showing the hyperfine structure. The black trace (top half of the figure) is the experimental data while the other coloured trace (bottom half of the figure) is a simulation using the model Hamiltonian.

listed bond lengths of 288.5 pm based on a CASSCF study, 282.9 pm calculated at the BP86/QZ4P level of theory, and 277.2 pm using a two-component MRCIS calculation.^{11,12,14} This latter result clearly showing that high-level calculations are required to model the electronic structure associated with PbI. Apart from the computational study by Li *et al.*, no other work has been reported on the bond length of SnI but it follows the trend expected in going from SnF, SnCl, SnBr to SnI.

Born-Oppenheimer breakdown (BOB)

BOB has been observed in a number of transition metal and rare-earth metal systems via analysis of their spectroscopic

constants. Species such as ZrO, ZrS, and PtS have all shown manifestations of BOB via analysis of the equilibrium bond lengths of the different isotopologues.^{29,30} In comparing the r_e values of ^{208}PbI , ^{206}PbI , and ^{207}PbI , they all agree to be within error which would imply that effects from BOB are most probably not being observed. Bond lengths obtained from the equilibrium parameter analysis of the ^{120}SnI , ^{116}SnI , and ^{118}SnI isotopologues show that they agree to be within error which also implies the effects of BOB are most probably not being observed.

In an attempt to evaluate if effects from BOB could be observed for PbI or SnI, a multi-isotopologue fit was carried out using the Dunham expression given in Equation (3) where

TABLE II. Derived equilibrium parameters for ^{120}SnI , ^{118}SnI , and ^{116}SnI in the $X^2\Pi_{1/2}$ electronic state.

Parameter ^a	^{120}SnI	^{118}SnI	^{116}SnI	Literature
Y_{01}/MHz	1 121.766 76(38)	1 131.554 27(38)	1 141.675 58(57)	
Y_{11}/MHz	-2.991 96(12)	-3.031 18(15)	-3.072 74(30)	
Y_{21}/kHz	1.057(12)	1.080(18)	1.208(52)	
Y_{02}/Hz	-160.6(31)	-167.7(31)	-159.7(47)	
p_{00}/MHz	287.530 6(46)	290.064 8(46)	292.681 8(72)	
p_{10}/MHz	-2.014 6(11)	-2.050 8(12)	2.091 8(26)	
a_{00}/MHz	225.064(98)	225.50(10)	224.91(16)	
a_{10}/MHz	-0.940(24)	-1.076(26)	-0.964(64)	
d_{00}/MHz	100.756(34)	100.620(32)	100.520(56)	
d_{10}/MHz	-1.370(10)	-1.3192(92)	1.240(26)	
eQq_{00}/MHz	-696.10(26)	-697.51(27)	-696.15(49)	
eQq_{10}/MHz	-2.537(66)	-2.158(73)	-2.57(17)	
r_e/pm	270.323 453(46)	270.323 424(45)	270.323 434(67)	269.7 ^b
ω_e/cm^{-1}	197.8(19)	196.0(18)	203.6(3.0)	199, ^c 204 ^b
$\omega_e x_e/\text{cm}^{-1}$	0.419 8(57)	0.415 9(54)	0.439 9(91)	0.55 ^c
D/cm^{-1}	23 293(549)	23 113(521)	23 568(849)	20 018, ^b 19 550 ^c
No. of lines	458	404	264	
RMS error	1.05	0.95	1.14	

^aThe numbers in brackets indicate one standard deviation.

^bReference 13.

^cReference 19.

in the Dunham formalism each $Y_{ij} = Y_{ij}^\alpha$, where

$$Y_{ij}^\alpha = U_{ij} \mu_\alpha^{-(i+2j)/2}, \quad (4)$$

where U_{ij} is a Dunham isotope-independent parameter and μ_α is the reduced mass of the isotopologue α . At the precision of the current experiment, BOB, if any, will only be observed for Y_{01}^α and so Equation (4) becomes

$$Y_{01}^\alpha = U_{01} \mu_\alpha^{-1} - \delta_{01}^M - \delta_{01}^I. \quad (5)$$

The metal (M) correction term is given by Watson^{31,32} with the relation

$$\delta_{01}^M = \frac{-U_{01} \Delta_{01}^M m_e}{\mu_\alpha M_M}, \quad (6)$$

where Δ_{01}^M is the electronic BOB parameter for Sn or Pb, m_e is the rest mass of an electron, and M_M is the mass of a given Sn or Pb isotope.

The results of the fits are given in Table III in which the Dunham isotope-independent parameter U_{01} , can easily be derived using Equations (5) and (6). The isotopically independent Born-Oppenheimer (BO) bond lengths have been determined for both SnI and PbI. The BOB parameter Δ_{01}^M is given in Table III. For SnI, Δ_{01}^{Sn} was found to be small and indeterminable indicating that BOB is not being observed for this species which agrees with the previous assessment based on the equilibrium bond lengths of the different isotopologues. In the final fit on SnI, Δ_{01}^{Sn} was fixed to zero and it had no effect on the standard deviation of the fit. Looking at the electronic spectra of the other tin monohalide species, no low lying electronic states have been observed except for the $X^2\Pi_{3/2}$ states which are $\sim 2400 \text{ cm}^{-1}$ higher in energy than the $X^2\Pi_{1/2}$ electronic state with the next lowest electronic state being over 15000 cm^{-1} higher in energy so it is unlikely that coupling between electronic states is happening to the degree that

would result in BOB.^{19,20,33,34} It would be worthwhile to make a comparison of the BOB parameter with that obtained from SnCl, which has been studied previously using microwave spectroscopy. Unfortunately only transitions from the ground vibrational states of the different isotopologues were observed making a robust analysis of the BOB parameters impossible.²¹

For PbI, because of the additional hyperfine splitting associated with ^{207}PbI , only the ^{208}PbI and ^{206}PbI species were included in the initial fit resulting in $\Delta_{01}^{\text{Pb}} = +18.5$ which is significantly large and needs further consideration. Since iodine has only one isotope, the BOB parameter for this was not included in the fits for PbI.

To check if the result from the initial fit is valid as only two isotopologues (^{208}PbI and ^{206}PbI) were included in the fit, an alternative multi-isotopologue fit was carried out where the fitted rotational constants from each vibrational state and for each isotopologue (including ^{207}PbI) were used to calculate a split-free transition. If we treat the species as a $^1\Sigma$ state, then this split free transition was then used in a fit involving only six terms, including Y_{01} , Y_{11} , Y_{21} , and Y_{02} and the BOB parameter, Δ_{01}^{Pb} . The results from this fit gave the same value for Δ_{01}^{Pb} as calculated in the original fit with just the ^{208}PbI and ^{206}PbI species.

It is unlikely that the Δ_{01}^{Pb} value is indicating BOB within PbI since for metal containing species, the value of Δ_{01}^M usually comes out negative (see Table IV in Ref. 30). Therefore, the fitted BOB parameter for PbI is most likely representing a field-shift effect as noted by Tiemann *et al.* and Giuliano *et al.* and has been seen before in lead containing compounds (e.g., PbSe and PbTe^{35,36}). As there is only one isotope for iodine, a more robust analysis is not possible. It has been shown that for species MX, $\Delta_{01}^M \approx \Delta_{01}^X$,³² however, given the size of field-shift effects seen in Pb containing species such as PbSe and PbTe, this approximation is not valid unless the field-shift terms (V_M and V_X) are incorporated into the fit. The

TABLE III. Isotopic dependent equilibrium parameters for PbI and SnI, in the $X^2\Pi_{1/2}$ electronic state.

Parameter ^a	SnI	PbI ^b	Isotope dependence ^c
Y_{01}/MHz	1 121.766 97(23)	819.341(13)	μ^{-1}
Y_{11}/MHz	-2.992 044(78)	-2.035 80(15)	$\mu^{-3/2}$
Y_{21}/kHz	1.064 4(88)	0.282(29)	μ^{-2}
Y_{02}/Hz	-162.0(20)	-93.2(10)	μ^{-2}
$\delta_{00}(\text{Sn/Pb})/\text{MHz}$...	-0.040(13) ^c	$\mu^{-1} M_{\text{Sn/Pb}}^{-1}$
p_{00}/MHz	287.550 6(28)	327.193 4(34)	μ^{-1}
p_{10}/MHz	2.021 24(76)	1.976 76(72)	$\mu^{-3/2}$
a_{00}/MHz	225.106(64)	187.179(47)	g_N
a_{10}/MHz	-0.967(18)	-0.630(34)	$g_N \mu^{-1/2}$
d_{00}/MHz	100.690(22)	239.401(12)	g_N
d_{10}/MHz	1.337(68)	0.722(16)	$g_N \mu^{-1/2}$
eQq_{00}/MHz	-696.62(17)	-700.592(53)	Q
eQq_{10}/MHz	-2.384(49)	-2.040(67)	$Q \mu^{-1/2}$
$U_{01}/\text{MHz amu}$	69 159.178(14)	64 575.0(10)	
$\Delta_{01}^{\text{Sn/Pb}}$	0	18.5(60)	
$r_e^{\text{BO}}/\text{pm}$	270.323 428(27)	279.753 6(22)	
No. of lines	1 218	693	
RMS error	1.14	1.08	

^aThe numbers in brackets indicate one standard deviation.

^bUsing data from only ^{208}PbI and ^{206}PbI .

^c ^{120}SnI and ^{208}PbI were used as the reference isotopologues.

lack of additional isotopic information for iodine would result in strong correlation between parameters and make evaluation of both the BOB and field-shift effects impossible without prior assumptions. In addition, the level of precision required to do an analysis of this type is probably not obtainable using the CP-FTMW spectrometer used in this study and additional work would need to be done on a cavity-FTMW system in order to improve the precision of the rotational and centrifugal distortion constants. It would also be useful to compare our results with PbCl (or PbBr) in which BOB parameters for both Pb and Cl could be evaluated and field-shift effects could be taken into account. Although work on PbF and PbCl has been carried out using microwave spectroscopy, the BOB parameters associated with both species have yet to be evaluated due to only the ground vibrational state transitions being observed.^{6,8}

Vibrational frequencies and dissociation energies of Pbl and SnI

The harmonic vibration frequency, ω_e , and the vibrational anharmonicity constant, $\omega_e x_e$, of Pbl were estimated using the relations developed by Kratzer³⁷ and Pekeris,³⁸ respectively. These assume a Morse potential where $Y_{01} \approx B_e$, $Y_{02} \approx -D_e$, and $Y_{11} \approx -\alpha_e$ (see Tables I and II),

$$\omega_e \approx \sqrt{\frac{4B_e^3}{D_e}}, \quad (7)$$

$$\omega_e x_e \approx B_e \left(\frac{\alpha_e \omega_e}{6D_e^2} + 1 \right)^2. \quad (8)$$

The dissociation energy, D , can be approximated by the relation³⁹

$$D \sim \frac{\omega_e^2}{4\omega_e x_e}. \quad (9)$$

These expressions have been found to provide reasonable estimates of ω_e , $\omega_e x_e$, and D for a number of different systems including AuCl, PtCl, and ScCl.^{40–42} For Pbl, the harmonic frequency is in good agreement with the result from the electronic study of Rodriguez *et al.* in 1996 (160.3 ± 0.6 cm⁻¹).¹⁰ The value for the anharmonicity constant, $\omega_e x_e$, differs considerably from the value of Rodriguez *et al.* (0.24 ± 0.03 cm⁻¹); however, this difference could arise from the low resolution of the earlier study ($\Delta\lambda = 0.15$ nm). For Pbl, there have been several computational chemistry studies carried out; the work of Benavides-Garcia and Balasubramanian determined the value of ω_e to be 153 cm⁻¹, which is on the low side of the experimental value, and a D value of 20486 cm⁻¹ which is in good agreement with the values estimated using Equation (9); however, it is significantly different from the experimental value of 16088 ± 700 cm⁻¹.^{11,43} The work by Stoll *et al.* calculated ω_e to be 168 or 169 cm⁻¹ and values of D of 14598 and 23954 cm⁻¹ depending on the method used.¹⁴ Li *et al.* calculated ω_e to be 174 cm⁻¹ and a D value of 16937 cm⁻¹ while including a spin-orbit correction. Ziebarth *et al.* assigned the upper limit of D to be 20405 cm⁻¹.^{9,13} The varying values of D indicate further experimental study is required to ascertain with better certainty the value of D for Pbl.

Not much is known about the ground state of SnI except that the constants ω_e (199 cm⁻¹) and $\omega_e x_e$ (0.55 cm⁻¹) have been determined experimentally and they compare well with results obtained in this work.¹⁹ If we use the values obtained by Oldershaw and Robinson with Equation (9), a dissociation energy of ~ 18000 cm⁻¹ is obtained which is lower than that estimated in this study (23293 cm⁻¹). Other experimental studies have determined the dissociation energy to be ~ 19650 cm⁻¹ while the computational study by Li *et al.* puts the D for SnI at ~ 22019 cm⁻¹ which is closer to the result of this study.^{13,44}

Lambda doubling and hyperfine constants of Pbl and SnI

As seen in Tables I and II, the Λ -doubling constant p has been determined for both Pbl and SnI. The constant p can be expressed as follows:

$$p_v = 2 \sum (-1)^s \frac{\langle \Pi | A_v L_+ | \Sigma^s \rangle \langle \Sigma^s | A_v L_- | \Pi \rangle}{E_\Pi - E_\Sigma}. \quad (10)$$

In this equation s is even and odd for Σ^+ and Σ^- states, respectively. For ²⁰⁸Pbl, $p = -326.2$ MHz which would imply that the interaction is with a Σ^+ state. The lowest lying Σ^+ state for Pbl is at 22529 cm⁻¹.¹⁰ Using this value and assuming only one Σ state is contributing, then p is calculated to be approximately -600 MHz which would imply there is some quenching of the Λ -doubling in Pbl. A reason for this quenching has been put forward by Ziebarth *et al.* in which they suggested that it is probably due to the cancellation of the $A^2\Sigma^+$ state with a nearby $^2\Sigma^-$ state arising from the $3\sigma 2\pi^2$ configuration.⁹ This hypothesis is supported by the theoretical work of Benavides-Garcia and Balasubramanian.¹¹

For ¹²⁰SnI, $p = +286.6$ MHz, which would imply that the interaction is with a Σ^- state. In the work by Murthy *et al.* and Oldershaw and Robinson, two bands with Σ symmetry, the $A^2\Sigma$ state at 17917 cm⁻¹ and the $B^2\Sigma$ state at 32173 cm⁻¹ were analysed.^{18,19} If we assume only one Σ state is contributing then p is calculated to be 301.23 MHz for the $A^2\Sigma$ state and 167.6 MHz for the $B^2\Sigma$ state. Electronic studies of SnF, SnCl, and SnBr have found that the lowest lying Σ state is actually a Σ^+ state and not a Σ^- state.^{45–47} In the case of SnCl, the Λ -doubling parameter p is -276.8 MHz which does imply that a Σ^+ state is the cause of the interaction. If it were assumed that the interaction within SnI is also with a Σ^+ state, as in Pbl, this would imply significant quenching resulting from a nearby Σ^- state. For SnCl, the nearest Σ^- state is the $a^4\Sigma^-$ state at 27622 cm⁻¹ so this state would need to be much lower in energy in order for it to have significant quenching effects in SnI.³³ Additional electronic spectroscopic work and computational chemistry calculations need to be carried out on SnI in order to investigate this further.

The ¹²⁷I hyperfine splitting was modelled with the a and d Frosh and Foley parameters,⁴⁸

$$a(\text{in MHz}) = \frac{\mu}{4\pi} \frac{2g_N \mu_B \mu_N \left\langle \frac{1}{r^3} \right\rangle_L}{h \times 1 \times 10^6}, \quad (11)$$

$$d(\text{in MHz}) = \frac{3\mu}{8\pi} \frac{g_e g_N \mu_B \mu_N \left\langle \frac{\sin^2 \theta}{r^3} \right\rangle_S}{h \times 1 \times 10^6}. \quad (12)$$

In Equations (11) and (12), μ is the magnetic constant, g_N is the nuclear magnetic dipole moment divided by the nuclear spin number (nuclear g -factor), μ_B is the Bohr magneton, μ_N is the nuclear magneton, and g_e is the electron spin g -factor. The Frosh and Foley parameters can be used to determine the expectation value of $\Sigma_n \langle 1/r_n^3 \rangle_{L \text{ or } S}$, where S relates to the spin wavefunction and L the orbital wavefunction. The nuclear spin orbital constant, a , is proportional to $\langle 1/r^3 \rangle_L$, where r is the average distance between the orbiting electrons and the nucleus possessing the spin I . For the iodine atom, $\langle 1/r^3 \rangle_L = 162.80 \times 10^{30} \text{ m}^{-3}$, which basically represents the electron-nuclear separation for a $2p$ electron. The $\langle 1/r^3 \rangle_L$ value for ^{208}PbI is $11.77 \times 10^{30} \text{ m}^{-3}$ which is over an order of magnitude smaller indicating that the unpaired electron contributing to a is located on average much further away from the iodine nucleus. A similar result is found for ^{120}SnI with $\langle 1/r^3 \rangle_L = 14.15 \times 10^{30} \text{ m}^{-3}$. It was found with group 4 monochloride species that there is a decrease in the $\langle 1/r^3 \rangle_L$ value for the Cl nucleus when going down the group with the unpaired electron being located further away for the heavier elements. Not surprisingly a similar trend is seen here. In terms of the magnetic hyperfine parameter d , as the c Frosh and Foley parameter was not fitted, $\langle 1/r^3 \rangle_S$ cannot be evaluated on its own but $\langle \frac{\sin^2 \theta}{r^3} \rangle_S$ can be evaluated. For ^{208}PbI , $\langle \frac{\sin^2 \theta}{r^3} \rangle_S = 10.03 \times 10^{30} \text{ m}^{-3}$ while for ^{120}SnI , $\langle \frac{\sin^2 \theta}{r^3} \rangle_S = 4.22 \times 10^{30} \text{ m}^{-3}$. A similar trend in $\langle \frac{\sin^2 \theta}{r^3} \rangle_S$ was seen in PbCl and SnCl , where it was proposed that relativistic effects associated with Pb could be the reason for the increase in the $\langle \frac{\sin^2 \theta}{r^3} \rangle_S$ value in going from SnCl to PbCl . This increase in relativistic effects results in a slightly less ionic bond (or less spin density on I) in PbI than SnI .^{8,21}

Nuclear quadrupole coupling constants and ionicity

Very precise NQCCs have been obtained for the iodine nucleus for both PbI and SnI . The NQCCs of the iodine nucleus, as seen with other species, show a significant dependence on the vibrational state. The equilibrium NQCC for PbI and SnI can be found in Tables I and II.

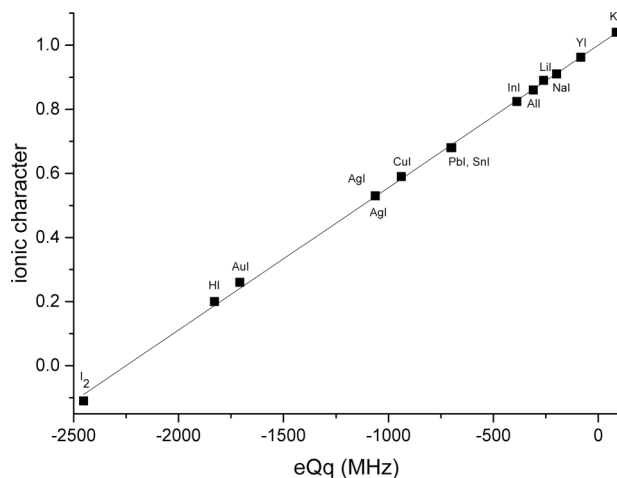


FIG. 3. Plot of ionic character vs $eQq(\text{I})$ using $i = 1 + \frac{XZ}{eQq_{n10}}$ for various I containing species. Displayed results include data from this work and Refs. 49–56.

The ionic character of the PbI and SnI bonds can be estimated from the halogen NQCC. If contributions from the d -orbitals of I are neglected in the bonding orbitals, the ionic character can be related to the coupling constants by³⁹

$$i_c = 1 + \frac{eQq_0(X)}{eQq_{n10}(X)}, \quad (13)$$

where eQq_{n10} is the NQCC for a singly occupied np_z ($n = 5$) orbital for atomic I ($eQq_{510} = +2209.1 \text{ MHz}$).³⁹ For PbI and SnI , the ionic character $i_c \sim 0.69$. Figure 3 shows a plot of the predicted ionic character of other I containing molecules. No experimental results are available for $eQq(\text{I})$ for the other group 4 elements (e.g., Cl , SiI , and GeI) and so a look at the trend down this group is not possible. It can be seen that both Pb and Sn have a similar ionic character consistent with studies of SnCl and PbCl .^{8,21}

CONCLUSION

We report for the first time the pure rotational spectra of PbI and SnI . Spectroscopic parameters including rotational constants, centrifugal distortion constants, Λ -doubling constants, magnetic hyperfine constants, and nuclear quadrupole coupling constants have been evaluated for a number of different isotopologues and vibrational excited states for each species. Due to the recording of excited vibrational state data, accurate equilibrium constants have been evaluated. The equilibrium bond lengths agree well with the results from a number of computational studies. Evaluation of harmonic frequencies and dissociation energies has also been carried out with the values of ω_e agreeing well with computational studies; however, for PbI , there was some disagreement in the D evaluated based on the equilibrium parameters compared to the experimental determined value. A multi-isotopologue analysis was carried out in order to investigate if effects from BOB could be observed. For SnI , the BOB parameter proved too small to reach a suitable conclusion, while for PbI the BOB parameter indicated that a nuclear field-shift effect was occurring and not BOB. Analysis of the hyperfine constants showed the bonding for both SnI and PbI was ionic in nature with an ionic character of 69%. It is hoped that this work will help in assessing the potential of PbI and SnI as molecules that could be used in the measurement of the $e\text{EDM}$.

ACKNOWLEDGMENTS

We thank the European Research Council for postdoctoral fellowships awarded to D.P.Z. and S.L.S., and for project funding (No. CPFTMW-307000). D.P.Z. thanks Newcastle University for the award of a Faculty of SAGE Research Fellowship. Thanks to Bob Le Roy for conversations regarding PbI and SnI .

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